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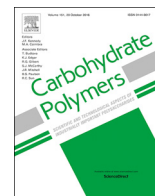
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A new way to improve physicochemical properties of potato starch

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ABSTRACT

Starch is an important class of macromolecules for human nutrition. However, its rapid digestibility leads to a high amount of glucose released into the blood and contributes to a high risk of obesity and type II diabetes. For these reasons, Heat-moisture treatment (HMT) of the starch was applied prior to complexation with linoleic acid to obtain a desired physicochemical properties while preserving its granular structure. The thermal properties, analyzed by DSC, implied that the HMT enhanced the formation of amylose-linoleic acid complexes, particularly when the complexation was succeeded at 70 °C. The viscosity behavior studied by RVA demonstrated a higher pasting temperature and lower peak viscosity due to less swelling. The granule-like structure remained after complexation at 70 °C for 30 min and followed by RVA to 85 °C. The combination of the HMT and linoleic acid addition improved the stability of the starch granules towards heating and shearing.

1. Introduction

Starch is the most abundant source of carbohydrates in nature. Starch can be found in all green plant tissues, including leaves, tubers, stems, roots, fruits, flowers, etc. Green plants produce starch for energy storage in a granular form. Starch is a polymeric carbohydrate composed of α -D-glucose units as a monomer. It is predominantly made of two types of polymers; amylose and amylopectin. Amylose is a linear polyglucan in which each glucose unit is linked via α -(1 \rightarrow 4)-glycosidic linkage, whereas, amylopectin is a branched polyglucan, composed of α -(1 \rightarrow 4)-glycosidic linkage of glucose molecules with some additional α -(1 \rightarrow 6) branch points (Ciric & Loos, 2013; Lewandowski, Co-investigator, & Lewandowski, 2015; van der Vlist et al., 2008, 2012). Amylose and amylopectin contribute about 98–99% of dry normal starch granules (Copeland, Blazek, Salman, & Tang, 2009; Manca, Woortman, Loos, & Loi, 2015; Manca, Woortman, Mura, Loos, & Loi, 2015). The rest of the components contain a small number of lipids, phosphate monoester, minerals, and protein/enzymes.

The utilization of starch is very broad, either in food products (for example: bakery, baby foods, ice cream, soup, sauce, confectionery, syrups, snacks, soft drinks, meat products, beer, fat replacers) or in non-food applications (for example: pharmaceuticals, cosmetics, detergents, fertilisers, bioplastics and textile, diapers, paper, adhesives, fabrics, packing materials, oil drilling) (Amagliani, O'Regan, Kelly, & O'Mahony, 2016; Copeland et al., 2009; Loos, Jonas, & Stadler, 2001; Loos, vonBraunmuhl, Stadler, Landfester, & Spiess, 1997; Konieczny &

Loos, 2018; Mazzocchi, Tsoufis, Rudolf, & Loos, 2014). As a food ingredient, starch supplies 50–70% of energy for a human diet and the glucose molecules provided by the starch metabolism is essentially used as a substrate in the brain and red blood cells (Copeland et al., 2009). The digestibility of starch determines the Glycemic Index (GI); the rate of glucose released into the blood. Unfortunately, a rapid rate of digestibility leads to a high GI, resulting in overweight and obesity, in the end contributing to some diseases, for example, type II diabetes (Soong, Goh, & Henry, 2013). The number of people with diabetes (adults 18+ years) in the world increased from 108 million in 1980 to 422 million in 2014 (World Health Organization, 2016). South-East Asia and the Western Pacific region contribute the largest numbers of people with diabetes. In the South-East Asia region, 17 million people in 1980 increased to 96 million people in 2014 (World Health Organization, 2016). By considering this, current international research is focused on starch and starchy foods.

Physical modification of starch by heat, moisture, radiation, or shear can be attractive since no chemical reagents are used, which is especially desirable for food products. Heat-moisture treatment (HMT) is one of the physical modifications that can alter the physicochemical properties of starch (pasting time, gelatinization, viscosity, swelling power, solubility, thermal stability, and crystallinity) without destroying the granular structure (Zavareze & Dias, 2011). The treatment involves the heating of starch at a high temperature (above the glass transition temperature T_g but below the gelatinization temperature at low moisture content (< 35%)) (Gunaratne & Hoover, 2002). Some

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studies show the effect of HMT on the molecular structure, functional properties and digestibility of starch (Gunaratne & Hoover, 2002; Liu et al., 2015; Senanayake, Gunaratne, Ranaweera, & Bamunuarachchi, 2014; Sharma, Yadav, Singh, & Tomar, 2015; Singh, Chang, Lin, Singh, & Singh, 2011; Van Hung, Chau, & Phi, 2016; Varatharajan et al., 2011). Molecular rearrangement occurred due to HMT, thus a Rapid Digestible Starch (RDS) was transformed into a Slowly Digestible Starch (SDS) and Resistant Starch (RS) (Wang, Zhang, Chen, & Li, 2016). Further treatment by inclusion complexes of a small guest molecule into the cavity of the amylose helix could be done to improve the indigestibility of the starch.

Food containing many carbohydrates is mainly consumed in the presence of lipid and protein. Lipid is known to form inclusion complexes inside the helix of amylose by hydrophobic interaction. The helical amylose-guest molecules inclusion complexes are called V-amylose (Seo, Kim, & Lim, 2015). Numerous studies have been carried out on complex formation and its physicochemical properties, involving amylose-polytetrahydrofuran complexes (Rachmawati, Woortman, & Loos, 2013), wheat starch-lysophosphatidylcholine (Ahmadi-Abhari, Woortman, Hamer, Oudhuis, & Loos, 2013; Ahmadi-Abhari, Woortman, Oudhuis, Hamer, & Loos, 2014), amylose-fatty acids (Seo et al., 2015), and starch-fatty acids (Arijaje & Wang, 2017; Kawai, Takato, Sasaki, & Kajiwar, 2012; Soong et al., 2013; Tang & Copeland, 2007; Zhou, Robards, Helliwell, & Blanchard, 2007).

Most studies of inclusion complexes have been performed on normal starches. Only a few studies combined HMT and inclusion complexation with a small guest molecule (Chang, He, Fu, Huang, & Jane, 2014). Chang et al. first dried corn starch, then adjusted the moisture content to 10–50% followed by heating at 80 °C for 12 h in a sealed stainless-steel reaction vessel. Lauric acid dissolved in ethanol was added to the pre-heated starch and further heated for 2 h at 80 °C. In our previous research we used various fatty acids (C8, C10, C12, C14, and C16) to form complexes with pure amylose and found that a longer chain length of fatty acids could form inclusion complexes with longer amylose fraction, hence a greater yield was achieved (Cao, Woortman, Rudolf, & Loos, 2015). In our current research we employed a longer chain of fatty acids - linoleic acid (C18:2) since it is liquid, thus emulsification could be achieved in water at room temperature. In addition, due to its unsaturation, linoleic acid is a better choice for a health-concerned application. It is also the main component of commonly used oil for foods, for example, sunflower oil and olive oil.

Tween 80 (Polyoxyethylene sorbitan monooleate) and span 80 (sorbitan monooleate) are used as nonionic surfactants, offering some advantages in their application (Hong, Kim, & Lee, 2018). They are stable in alkaline, acids, and electrolyte, flexible to formulate based on a required Hydrophilic-Lipophilic Balance (HLB) of an oil phase, safely used in food, cosmetics, and pharmaceutical application, and they could increase the stability of O/W and W/O emulsion (Hong et al., 2018). In addition, tween 80 and span 80 are known as a good emulsifier for unsaturated fatty acids (Croda Europe Ltd., 2009). The combination of emulsifiers having high HLB and low HLB value at appropriate weight ratio enhances the emulsification process compared to a single emulsifier (Croda Europe Ltd., 2009; Hong et al., 2018; Koneva et al., 2017). The weight ratio of tween 80 and span 80 for linoleic acid-water emulsion was calculated based on the required HLB value of linoleic acid (Croda Europe Ltd., 2009), and found that 1:3 was the optimum ratio. Our current research was focused on the heat-moisture treatment of potato starch with a moisture content of 13.4%, heated till 115–145 °C prior to complexation with linoleic acid in a tween 80 and span 80 – water system (see Figs. S1 and S2 for the experimental scheme).



Fig. 1. Pressure Vessel for preparing heat-moisture treated starch.

2. Materials and methods

2.1. Materials

Normal potato starch (NPS) with a moisture content of 13.4%, linoleic acid technical (LA) 60–74% (GC) with density 0.902 g/mL, tween 80 viscous liquid with a density of 1.064 g/mL, span 80 with a viscosity of 1000–2000 mPa s at 20 °C and density of 0.986 g/mL at 25 °C, lugol (iodine solution for microscopy), and calcium chloride dihydrate (A. C. S. reagent $\geq 99\%$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) were all purchased from Sigma-Aldrich Chemical Company.

2.2. Preparative heat-moisture treated potato starch (HPS)

The closing ring and cover of the self-made pressure vessel were preheated on a hot plate above 100 °C. The pressure vessel with a diameter of 2 cm and a height of 11 cm was almost fully filled with normal potato starch powder (13.4% moisture) and covered properly (see Fig. 1). The sample was heated to 115 °C to obtain HPS-115. Upon reaching 115 °C, the pressure vessel was removed and immediately cooled in a water bath until the ambient temperature was achieved. Afterwards, the cover was opened and the sample removed from the pressure vessel and stored for further treatment. The same procedure was also performed by heating normal potato starch until 125, 135 and 145 °C to obtain HPS-125, HPS-135, and HPS-145.

The moisture content was determined with a moisture analyzer (Sartorius MA35M, Sartorius AG, Gottingen, Germany).

2.3. Thermal analysis

Thermal analysis on the samples was conducted using a Perkin Elmer Pyris 1 Differential Scanning Calorimetry (DSC), which was calibrated with indium (melting temperature = 156.6 °C, and enthalpy = 28.45 J/g). A certain amount of NPS (without linoleic acid) at 13.4% and at 80% moisture content was weighed separately into the pan and sealed afterwards. An empty pan was used as a reference. The heating rate was 10 °C/min. The heating scan was performed from 20 °C

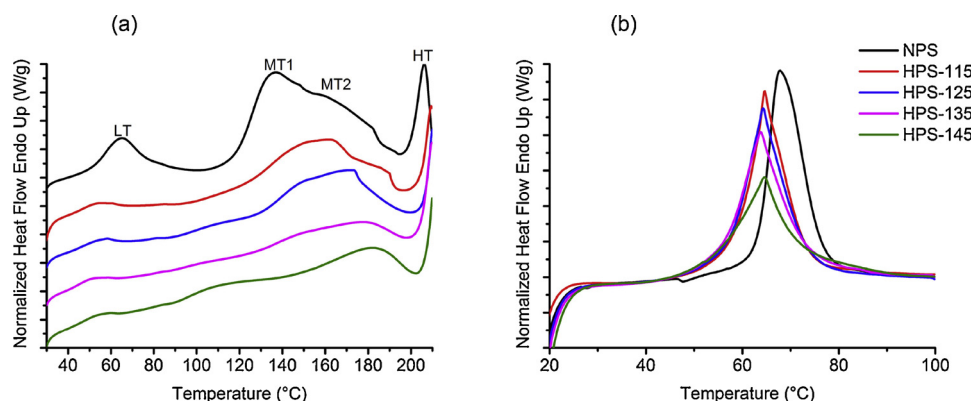


Fig. 2. DSC heating profiles from potato starch at a moisture content of 13.4% (a) and 80% (b) before (black curve) and after HMT until 115, 125, 135 and 145 °C in a pressure vessel.

Table 1

Thermal properties of 20% normal (NPS) and heat-moisture treated (HPS) potato starch before and after complexation with linoleic acid (LA) at room temperature or 70 °C.

Samples	Starch			Amylose – LA	
	Onset (°C)	Peak (°C)	ΔH (J/g)	Peak (°C)	ΔH (J/g)
NPS	61.5	66.4	25.5	–	–
HPS-115	56.7	63.2	19.5	–	–
HPS-125	54.9	62.9	17.8	–	–
HPS-135	53.6	62.2	16.4	–	–
HPS-145	52.2	63.1	12.8	–	–
NPS – LA	61.7	66.6	24.8	95.2	1.5
HPS-125 – LA	57.6	64.4	17.7	99.1	2.5
HPS-125 – LA at 70 °C	46.8	59.3	1.8	100.4	4.0
HPS-145 – LA	51.7	64.0	11.9	99.7	3.7
HPS-145 – LA at 70 °C	45.9	58.0	2.3	99.1	4.7

to 210 °C for samples with a moisture content of 13.4% and from 10 °C to 100 °C for suspensions with 80% moisture. Simulated tap water (a solution of 0.2621 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in distilled water) was employed in this research. The same procedure was also used for HPS-115, 125, 135 and 145. The measurements of all the samples were done in duplicate. The thermal properties were analyzed using DSC software (Pyris series, Perkin Elmer Version 8).

To study the thermal properties of complexes in an aqueous starch system, 20% (w/w) of the potato starch suspension in simulated tap water with an additional 3% emulsifier (combination of 25% of tween 80 and 75% of span 80) and 5% of linoleic acid based on dry matter (dm) of potato starch were mixed. The emulsion was prepared using a rotor/stator homogenizer (Polytron PT 1300 D, Kinematica, Lucerne, Switzerland) at 10,000 rpm for 5 min. The starch suspensions were rotated at 50 rpm for an hour at room temperature. The suspensions were pipetted into stainless steel pans from Perkin Elmer and scanned from 10 °C to 160 °C at 10 °C/min. Other samples were initially held at 70 °C for 30 min and scanned with the same temperature range and rate. All samples are measured in duplicate.

2.4. Pasting time and viscosity measurement

The viscosity behavior was analyzed using a Rapid Visco Analyzer RVA-4 Newport Scientific (NSW, Australia). Potato starch suspensions were prepared by mixing 9% starch on dm in simulated tap water with an additional 3% emulsifier (combination of 25% tween 80 and 75% span 80) and 5% linoleic acid based on the dry matter (dm) of potato starch. The emulsions were previously dispersed using a rotor homogenizer at 10,000 rpm for 5 min. The total weight of the samples was 28.0 g. The suspensions were equilibrated for 15 min at room

temperature before starting the RVA. The RVA profile was arranged as follows: equilibrating at 50 °C for 1 min, heating to 95 °C at 6 °C/minute, holding at 95 °C for 5 min, cooling to 50 °C at the same rate and holding at 50 °C for 2 min. The rotation speed was 960 rpm for the first 10 s and 160 rpm for the rest.

Some samples were previously heated in the RVA at 70 °C for 30 min. Subsequently, the RVA profile, as above, was executed by heating to 95 or 85 °C. Samples after heating at 70 °C for 30 min were also freeze-dried, ground into finer parts with a mortar and pestle, and stored for XRD analysis.

2.5. Swelling power

Swelling power of starch using 5% of linoleic acid and 3% emulsifier (combination of 25% tween 80 and 75% span 80) based on dry matter (dm) of potato starch was conducted at a different temperature (70 °C, 85 °C and 95 °C). The swelling power was measured based on the volume of precipitated particles according to a method of (Ahmadi-Abhari et al., 2013).

2.6. Starch crystallinity

An X-ray diffractometer (D8 Advance, Bruker, Germany) was employed to study the crystallinity of starch. The starch powder was packed compactly in the sample holder. The scanning was performed over 2θ range of 5–50° with an interval of 0.02° at 1 s per step. The voltage was 40 kV and the current was 40 mA using $\text{CuK}\alpha$ at a wavelength of 1.5418 Å as a source of radiation.

2.7. Granular structure

Starch granules were observed using a Nikon light microscope (Nikon, Eclipse 600, Japan). Starch samples of NPS and HPS were dispersed in simulated tap water to obtain a 1% suspension and observed under the microscope. Starch samples, which were previously processed in the RVA, were diluted with simulated tap water to obtain a 1% suspension. 3 drops of iodine solution were added to the suspensions and kept for several minutes to equilibrate prior to analysis. The starch suspensions were observed under bright-field illumination of the microscope with a 10x resolution objective lens. The birefringences of starch samples were observed under polarized light microscopy. The images were captured using a Nikon camera (Nikon, COOLPIX 4500, MDC Lens, Japan).

3. Results and discussion

Heat treatment at low moisture content has been carried to improve the complexation of potato starch and linoleic acid at raised

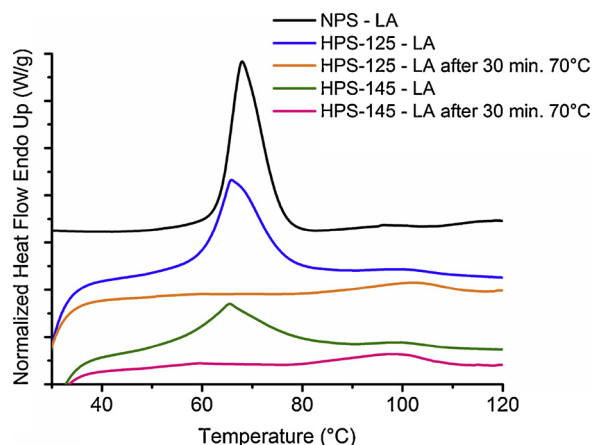


Fig. 3. DSC heating profile of 20% normal (NPS) and heat-moisture treated potato starch (HPS) after complexation with linoleic acid (LA) at room temperature and at 70 °C.

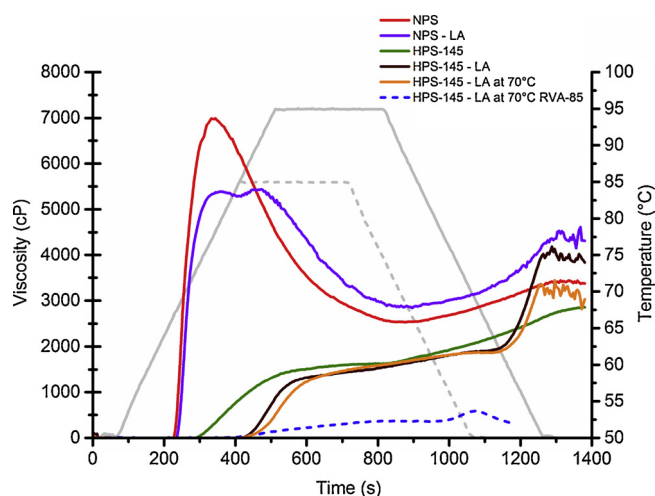


Fig. 4. RVA profile of 9% normal (NPS) and heat-moisture treated potato starch (HPS) at 145 °C (HPS-145) in simulated tap water before and after complexation with linoleic acid (LA) at room temperature and 70 °C.

temperature. Heat-moisture treated potato starch (HPS) has been successfully prepared, complexed with linoleic acid, and characterized. Normal potato starch (NPS) was used as a reference. The changes in physicochemical properties of HPS-LA were observed and compared to NPS.

Table 2

Pasting properties of 9% NPS and HPS suspensions before and after complexation in simulated tap water.

Sample	Pasting Temperature (°C)	Peak		Breakdown (cP)	Final Viscosity (cP)
		Viscosity (cP)	Time (s)		
NPS	66.0	6989	344	4456	3374
HPS-115	66.6	3410	492	817	4044
HPS-125	66.8	2938	548	549	3761
HPS-135	68.0	2360	612	236	3435
HPS-145	72.8	^a	^a	^a	2857
NPS - LA	67.8	5437	472	2597	4314
HPS-125 - LA	70.6	3158	700	108	6050
HPS-145 - LA	86.8	^a	^a	^a	3834

^a Not determined.

Table 3

Swelling power of potato starch before and after heat-moisture treatment and inclusion complexation with linoleic acid at different temperatures in simulated tap water.

Samples	Q (mL/g)			
	T room	70 °C	85 °C	95 °C
NPS	1.6	17.9	38.0	51.7
NPS - LA	1.6	10.9	23.3	48.8
HPS-125	1.6	16.7	24.6	34.1
HPS-125 - LA	1.6	7.9	15.2	24.6
HPS-145	3.0	8.7	11.3	17.2
HPS-145 - LA	3.0	4.6	7.9	10.6

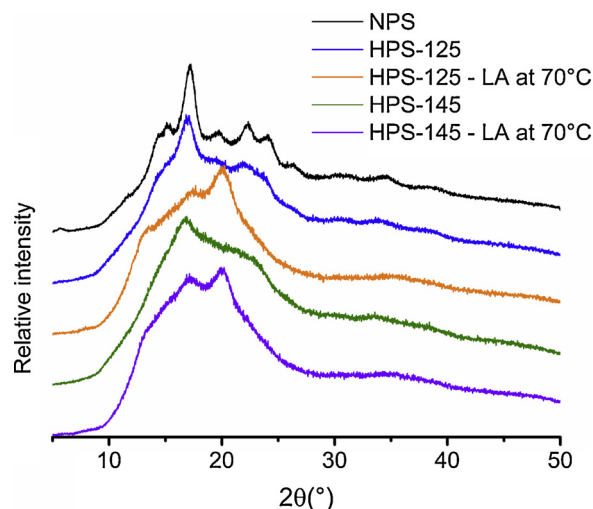


Fig. 5. XRD pattern of normal (NPS) and heat-moisture treated potato starch (HPS) after complexation with linoleic acid (LA).

3.1. Thermal analysis

Fig. 2a shows the influence of the heat-moisture treatment (HMT) at 115, 125, 135 and 145 °C (HPS-115, 125, 135, and 145) on normal potato starch (NPS) at 13.4% moisture on the DSC heating profile. The LT (sub- T_g) peak in NPS, which referred to the enthalpy of relaxation was, as may be expected, largely missing after the HMT. In Fig. 2a, the glass transition of HPS could be distinguished at approximately 100 °C after heating until ≥ 125 °C, which was not visible in NPS. The melting point of MT1, which is related to B-type crystallite, decreased at increasing HMT temperatures. This result suggests that the amorphous region was more present when the starch was heated. The slight shift of the HT endotherm to a higher temperature could be related to the loss of a very small amount of moisture during heating (Thiewes & Steeneken, 1997). Another possibility is that this shift can be explained

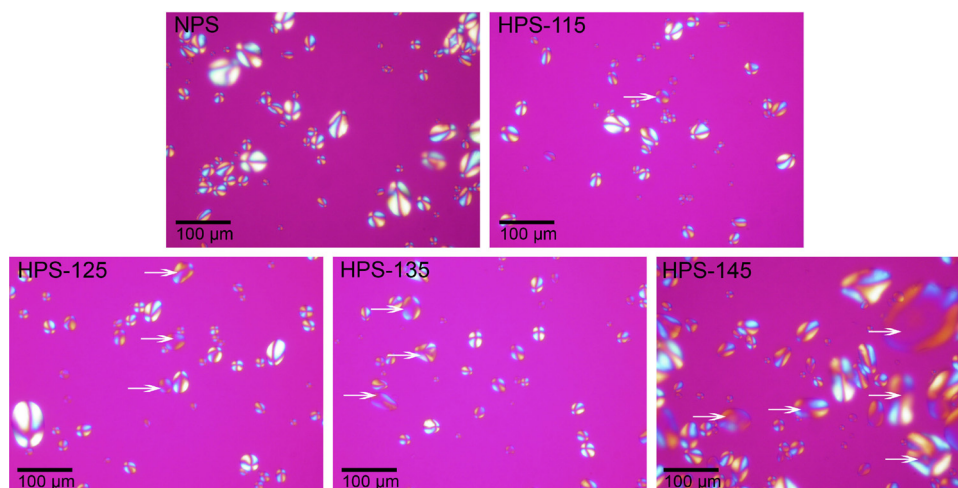


Fig. 6. Polarized light microscopy images with lambda filter of NPS and HPS in simulated tap water.

by a worse conductivity of the HPS due to a less dense packing of the starch granules. The lower density was proved by the fact that the sample amount of a full DSC pan was less for the HPS compared to NPS. The lower density of the HPS samples was due to some swelling and agglomeration of the particles.

Fig. 2b shows that with DSC measurements in excess of water, the endotherm peak, onset and endset temperatures (see Table 1) of the starch gelatinization decreased by the increased temperature of the HMT. There the majority of amylose-lipid complexation occurs during the gelatinization process (Ahmadi-Abhari et al., 2014), it may be expected that complexation with lipid will be easier. The reduction in ΔH of potato starch indicated the rupture of double helices or the crystalline region of the starch (Gunaratne & Hoover, 2002; Wang, Wang, Yu, & Wang, 2016).

The addition of linoleic acid lowered the enthalpy of the starch somewhat (first endotherm) and rose the enthalpy of the amylose-linoleic acid complexes (second endotherm) (see Fig. 3 and Table 1) which is in agreement with the effect of LPC addition in wheat starch (Ahmadi-Abhari et al., 2013). The amount of complexes formed in normal potato starch is quite low compared to another report (Kawai et al., 2012). The peak of the amylose-LA was observed at around 95 °C. More inclusion complexes with linoleic acid were formed at higher HMT temperature and also complexation at 70 °C for 30 min improved the complex formation (Table 1). The complexation at 70 °C was not performed on NPS because, due to gelatinization, sampling was not possible. The HMT caused the starch granules to partly gelatinize, while the whole structure remained intact. In addition, HMT forced the formation of more stable physical crosslinking in the granules, which improved the complexation at elevated temperatures without destroying the main structure. Furthermore, the use of tween 80 and span 80 enabled the formation of a stable linoleic acid-water emulsion system, which facilitated the complexation of linoleic acid into the hydrophobic cavity of amylose in starch. Our preliminary research of starch-tween 80 and span 80 suspensions in a DSC measurement displayed an insignificant second endotherm peak; hence the second endotherm peak appeared in Fig. 3 were mostly due to amylose-linoleic acid complexes. Research on corn starch (3% w/w) investigated the effect of tween 80 (0, 7.5, 15, 22.5 and 30 g/100 g of starch) and found that a resistant starch due to starch-surfactant complexes increased slightly after the addition of 7.5% of tween 80 and rose significantly after 15% of tween 80 (Vernor-Carter et al., 2018). In our study, the concentration of tween and span was far below (3%), thus the interaction of emulsifier and starch was negligible.

3.2. Pasting time and viscosity behavior

The effect of the heat-moisture treatment (HMT) on normal potato starch (NPS) and the influence of the linoleic acid (LA) addition on the RVA viscosity profile are shown in Figs. 4, S3 and Table 2. The pasting viscosity could be largely decreased and shifted to a higher temperature by the heat-moisture treatment. The higher the temperature during the HMT, the more the swelling of the starch granules was delayed and the peak temperature decreased. In HPS-145, the breakdown could not be determined. The increase in pasting temperature could be related to more physical cross-linkages formed among starch chains during the HMT, hence the amylose leaching was largely reduced and thus more heat was required to disintegrate the structure (Sharma et al., 2015). Furthermore, the reduction in breakdown indicated that the starch heat and shear stability was improved (Sharma et al., 2015; Zavareze & Dias, 2011). Moreover, the addition of linoleic acid clearly increased the pasting temperature further for the HPS, while this effect was small for NPS. The peak viscosity shifted to a later time for HPS and the breakdown decreased after complexation. During heating until 95 °C in the RVA, most parts of the starch were dissociated (see Table 1). When cooling to 50 °C, the dissociated amylopectin, amylose, and linoleic acid were rearranged and formed a new network of amylose-linoleic acid and amylose-amylopectin in aqueous solution (Chang et al., 2014). By heating the HPS and linoleic acid until 85 °C, and thereby preventing the amylose-linoleic acid complexes melted and leached from the starch granules, hence the final viscosity could be reduced.

3.3. Swelling power

Table 3 shows the swelling power of NPS and HPS at various conditions. At room temperature, the HPS starches had slightly more swelling compared to NPS. At a temperature of ≥ 70 °C, the swelling power of HPS was lower than NPS. This result was consistent with the pasting profile. The decrease in swelling power of HPS could be described by the amylose-amylose, amylose-amylopectin, and amylopectin-amylopectin interactions in which the number of free hydroxyl groups was reduced and less able to interact with water (Varatharajan, Hoover, Liu, & Seetharaman, 2010). The further reduction in swelling power with the addition of fatty acid could be explained by the formation of more stable helices of amylose-linoleic acid inclusion complexes, hence inhibiting the swelling capability of starch in water (Wang, Wang et al., 2016). Furthermore, the addition of fatty acids prior to gelatinization might have covered a part of the starch granules and increased the hydrophobicity of the starch, and thereby affected the water traveling into the starch granules (Zhou et al., 2007).

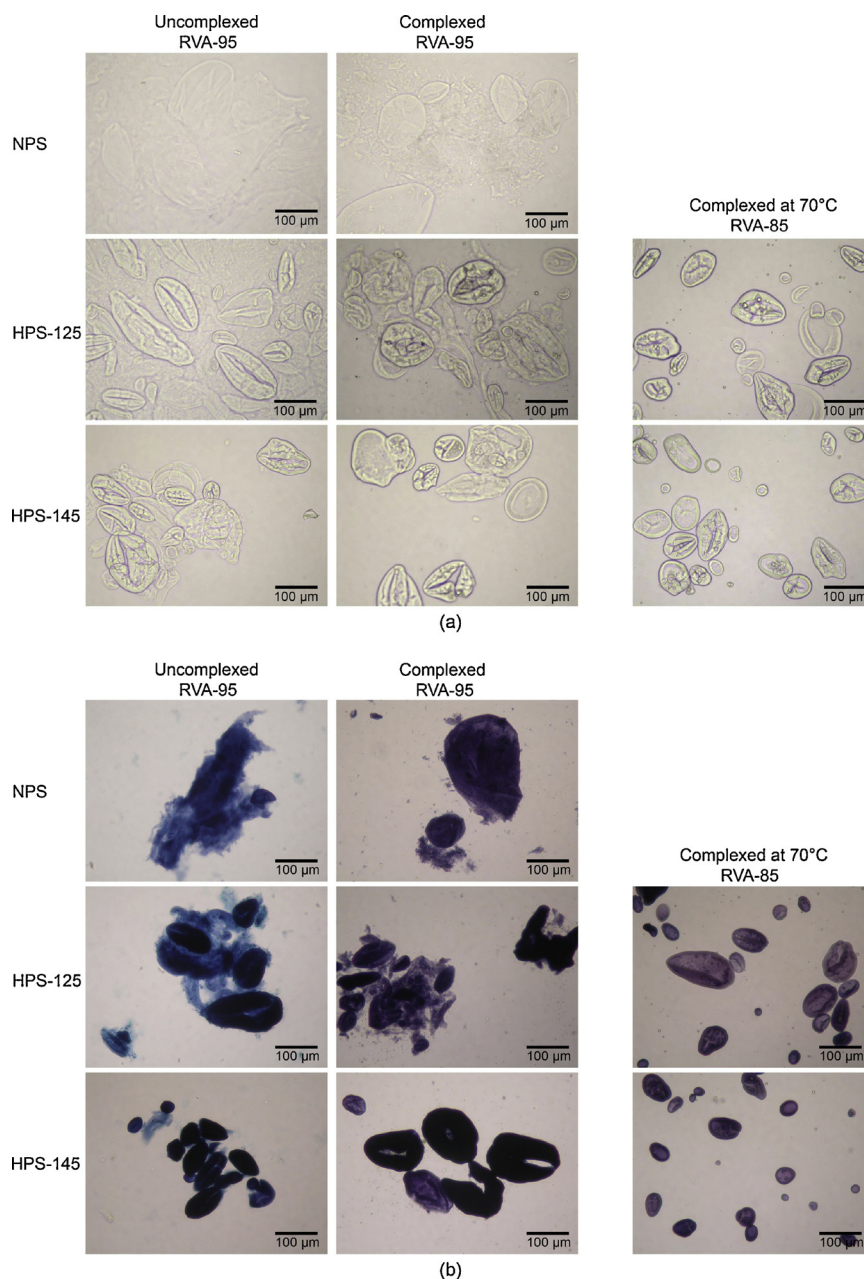


Fig. 7. Light microscopy images of NPS and HPS without and with complexation after the RVA measurement heated until 95 °C and 85 °C, (a) without and (b) with iodine staining.

3.4. XRD

The starch crystallinity was studied by using X-ray Diffraction (XRD). NPS exhibited a B-type crystalline pattern under XRD observation with reflections at 2θ of 5.5°, 15°, 17.1° and 22–24° (Varatharajan et al., 2010, 2011). The HPS showed decreasing in the diffraction peak, which could be attributed to the rearrangement of the double helices in a more irregular parallel crystalline pattern due to the rupture of hydrogen bonds as an effect of the heat-moisture treatment at a high temperature (Zhang et al., 2014). The crystallinity of potato starch reduced by HMT (Vermeulen, Goderis, & Delcour, 2006), which is also in agreement with our DSC results. HMT modified the XRD pattern from B-type to A- and B-type (Fig. 5). The reduction of the peak intensity at 2θ of 5.5° and 22–24°, and a broader peak at 2θ of 17° reflected the appearance of A- and B-type polymorphs (Ciric & Loos, 2013; Ciric, Oostland, de Vries, Woortman, & Loos, 2012; Varatharajan et al., 2010;

Ciric, Petrovic, & Loos, 2014; Ciric, Rolland-Sabate, Guilois, & Loos, 2014; Ciric, Woortman, & Loos, 2014; Ciric, Woortman, Gordiichuk, Stuart, & Loos, 2013). The addition of linoleic acid changed the pattern to a mixture of A-, B- and V-type (Fig. 5) in which the V-type crystallite was characterized by the reflection peak at 2θ of 7°–8°, 13° and 20° (Chang et al., 2014; Seo et al., 2015; Tang & Copeland, 2007; Zabar, Lesmes, Katz, Shimoni, & Bianco-Peled, 2009). However, the intensity at 2θ of 20° probably represented the single helices of linear starch chains crystallites rather than V-type amylose-lipid complexes (Varatharajan et al., 2010). The sharp decreasing of the double-helix amylopectin crystallinity was in harmony with the decreasing of the starch gelatinization enthalpy.

3.5. Granular structure

Starch granules exhibited a birefringence pattern (Maltese cross)

when it was observed under polarized light. This birefringence was attributed to the anisotropy phenomenon due to the ordered starch molecules of the crystalline region and disordered molecules of the amorphous region in the starch granules, in which the intensity depended on the relative crystallinity, microcrystalline orientation, and granular size (Wang, Zhang et al., 2016; Zhang et al., 2014). Birefringence indicated the average radial orientation of the helical structure (Chung, Liu, & Hoover, 2009). Fig. 6 shows the birefringence images of NPS and HPS. It is clearly observed that the intensity of the birefringence of HPS was less than NPS. For HPS, the higher the temperature of the heating, the less intensity of birefringence was detected, but not totally disappeared. The melting of the crystalline region after heating until the MT1 transition was not complete yet, thus some birefringence remained (Steeneken & Woortman, 2009; Vermeylen et al., 2006). The reduction of birefringence intensity was accompanied by the beginning of the gelatinization from the hilum (see white arrow in Fig. 6). The heat-moisture treatment increased the starch chains mobility, hence the radial orientation in the center of the granules is lost and consequently, this result suggests that the heat-moisture treatment disrupted the crystalline region of the starch, initializing from the hilum (the center part of the Maltese cross) to the outer part of the granules.

Fig. 7a shows that the starch granules of the NPS are largely ruptured and gelatinized after heating until 95 °C. The HMT reduced the swelling and the rupture of the starch granules due to physical cross-linking. Gelatinization occurred from the hilum, however the whole structure of the starch granules remained largely intact due to the HMT. The complexed samples observed after the RVA-95 don't show a large difference compared to the uncomplexed ones, which can be explained by the fact that the complexes melt at around 95 °C. The major effect was attained in HPS after complexation at 70 °C and heating until 85 °C in the RVA. Some small granules remained their shape. The “single” and less swelling granules could be distinguished in that condition. This result is in good agreement with the viscosity profile and the swelling power measurement above, which suggests that the starch gelatinization could be reduced with the heat-moisture treatment and the addition of linoleic acid. Among this condition, the samples kept their granular-like appearance. A study has been conducted on the effect of a heat-moisture treatment and inclusion complexation with lauric acid on cornstarch granules (Chang et al., 2014).

It is well-known that amylose contained in starch could be easily detected by the addition of an iodine solution to starch to form blue-colored inclusion complexes, in and outside of the granules (Langton & Hermansson, 1989). Fig. 7b shows starch granules of NPS, HPS-125 and HPS-145 stained with iodine after treatment in the RVA. It is clearly seen that without the addition of linoleic acid, the granules stained blue after the addition of iodine. The granules of NPS were totally disrupted, have an irregular shape after heating to 95 °C in the RVA, and the amylose partly leached out from the starch granules, whereas HPS-125 and HPS-145 showed that some granules retained their main structure. In the presence of linoleic acid, the leaching of the amylose could be hindered. This effect was more pronounced after complexation at 70 °C and when heating was limited until 85 °C in the RVA, in which the majority of the starch granules remained intact (see Fig. 7b). This can be explained due to the fact that 85 °C was below the melting temperature of the amylose-lipid complexes as could be concluded from the DSC measurements, while at 95 °C the complexes started to melt. For both NPS and HPS, the blue-stained granules turned into purple-stained granules after complexation with linoleic acid, in which shorter amylose chains could be included with iodine (Bailey & Whelan, 1961). This also confirmed that amylose-linoleic acid complexes were successfully formed.

4. Conclusions

The physicochemical properties of potato starch were observed that was treated by a combination of heat-moisture treatment and

complexation with linoleic acid. The heat treatment was conducted at low moisture and prior to the complexation. The results showed that due to the HMT, the starch granules partly gelatinized in the hilum while the main structure remained intact without noteworthy swelling due to more (stable) physically crosslinking. Hence the complexation improved, which was confirmed by the higher enthalpy of complexes at elevated temperatures without structure loss. The combination of heat-moisture treatment and inclusion complexation with linoleic acid could improve the heat and shear stability of the starch due to less swelling. The pasting shifted to a higher temperature and the viscosity could be lowered. Particularly when heating was limited until 85 °C, the starch granules largely remained in the granule-like appearance in suspension. The influence on the digestibility will be our future investigation.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.carbpol.2018.09.082>.

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